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Effects of co-combustion of biofuels on chlorine corrosion of furnace surfaces and prevention methods

Feasibility study

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Since the discovery of fire, energy has had an important role in everyday human life. From the sunlight to electricity, heat and transportation, the transformation of one form of energy into another form or useful work is present everywhere in the lives of modern people. It is projected that global consumption of energy will continue to rise, especially in developing countries and in developed countries with active heavy industry. In Finland, the energy consumption decreased by a few percent units from year the 2011 to the year 2012, and this trend is likely to persist if activity within the energy intensive heavy industry continues to decrease.

There are some problems related to energy production. Firstly, where and how the source of energy is produced and how it is transported around the globe. Secondly, combustion of fossil fuels releases flue gases of which many are classified as air pollutants. The most common ones are carbon dioxide, sulfur dioxide, nitrous oxides and particulate matter. These emissions affect the local air quality and contribute to global warming through the greenhouse gas effect.

However, modern combustion technology has enabled the replacement of fossil fuels with locally produced fuels and biofuels, such as peat and wood chips. The logistics of these fuels can possibly be much more sustainably and efficiently arranged and the greenhouse gas emissions can be smaller and or even negligible if biomass regrowth and carbon dioxide absorbance are considered

The aim of this Bachelor's thesis was to make a feasibility study of the changes to the mixture ratio of the peat and wood chips and to examine how this affects the formation of chlorine corrosion in the furnace at KELVO - bioenergy power plant. Kerava Energy's KELVO - bioenergy power plant is using a mixture of peat and wood chips as intended primary fuel with three different mixture ratios. The purpose of this thesis was to study if wood chips could only be combusted. However, plant-based fuels have a higher chlorine content than peat; thus this will cause chlorine corrosion because wood chips have a low sulfur content. When co-fired, peat and wood chips have such elemental attributes that they supplement each other to balance the sulfur-chlorine ratio so that the corroding effects of the mixture are negated.

Keywords	Corrosion, fuel, biofuel, FBC, Co-combustion

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Energialla on sitten tulen keksimisen jälkeen ollut tärkeä vaikutus ihmisten elämään. Auringonvalosta sähköön, lämpöön ja liikenteeseen, jonkin energiamuodon muuttaminen toiseen muotoon tai työksi on läsnä modernin ihmisen arkipäivässä. Energian kulutus tulee kasvamaan globaalisti, erityisesti kehittyvissä maissa ja runsaasti teollisuutta omaavissa kehittyneissä yhteiskunnissa. Suomessa energiankulutus laski muutaman prosenttiyksikön vertaillessa vuotta 2011 ja 2012, ja trendi luultavasti jatkuu jos raskaan teollisuuden aktiivisuus vähenee.

Energiantuotantoon liittyy kuitenkin ongelmia. Ensinnäkin, missä ja miten polttoaine on tuotettu ja miten se kuljetetaan loppukohteeseen. Toiseksi perinteisistä fossiilisista polttoaineista koituvat savukaasupäästöt jotka on luokiteltu ilmansaasteiksi. Yleisimpiä on hiilidioksidi, rikkidioksidi, typen oksidit ja pienhiukkaset. Nämä päästöt vaikuttavat lokaaliin ilmanlaatuun ja osallistuvat ilmaston lämpenemiseen kasvihuoneilmiön kautta.

Fossiiliset polttoaineet voidaan kuitenkin korvata paikallisesti tuotetuilla polttoaineilla, kuten turpeella ja metsähakkeella. Näiden polttoaineiden logistiikka on kestävää kehitystä ja tehokkuutta ajatellen järkevämpää ja kasvihuonekaasupäästöt vähäisempiä, tai biomassan jälleen kasvun takia päästöttömiä.

Tämän insinöörityön tarkoituksena on tehdä selvitys polttoaineen seossuhteen muutoksen vaikutuksesta kattilakorroosion muodostumiseen Keravan Energian KELVO - biovoimalaitoksella. Biovoimalaitoksella on käytössä yhdistelmäpolttoaineena turpeen ja metsähakkeen sekoitus kolmella eri sekoitus vaihtoehdolla. KELVOlla olisi tarkoitus kokeilla pelkästään metsähakkeen polttoa, mutta koska viheraineita sisältävä polttoaine on klooripitoisempaa kuin turve niin tästä saattaa seurata kloorikorroosiota, sillä metsähake ei sisällä niin paljoa rikkiä. Turve ja metsähake täydentävät alkuaineprofiileiltaan toisiaan kuitenkin niin, että rikki-kloorisuhde pysyy sellaisena ettei korrodoivia yhdisteitä pääse liiaksi syntymään.

Työn tarkoitus on myös selvittää mahdollisuuksia kattilakorroosion estoon.

Avainsanat	Kattilakorroosio, polttoaine, seospoltto, kerrosleijukattila

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I would like to thank everybody who has helped me to struggle this far. I am happy that this is done and it has ended. Big thanks to a few teachers and one internship engineer for their patience and support. And big thanks to my family for their effort.

Especially big thanks to the latest “gang” which we had, I had a lot of fun with you throughout the years. Also to a few special people with whom I got to know. Take care!

Contents

Nomenclature and abbreviations

Acid dew point	Temperature where water vapor condensates with sulfuric trioxide to form sulfuric acid
Alloy	A mixture of two metals
BFB	Bubbling Fluidized bed - boiler
Creep (deformation)	Metal fatigue and deformation
Eutectic alloy	Alloy with metal molar fractions such a way that the melting point of the mixture is the lowest possible
CHP	Combined heat and power - complete utilization of the heat value of given fuel
STP - conditions	Standard temperature and pressure, an IUPAC definition for certain temperature and pressure

1 Introduction

This Bachelor's thesis discusses the reasons for steam boiler chlorine corrosion and the procedures how to prevent it. The purpose of this thesis is to study whether it would be possible to make alterations to a fuel mixture in co-combustion of wood chips and peat in a BFB-boiler. The idea is to examine if it would be possible to change the fuel ratio to wood chips only and if this causes stronger wear on the power plant components in the form of corrosion. Both wood chips and peat have a different elemental composition, and their combustion causes different components to be released into the flue gas stream. Especially alkali metals are problematic within the context of high-temperature corrosion; they are found in fuels which are based on green plants, such as wood. High-temperature chlorine corrosion is prevented by co-combusting a fuel with a high enough sulphur concentration, such as peat. The lifetime of superheaters and the boiler in general is greatly reduced because of corrosion. [1, p. 179]

This thesis includes both the theoretical background to approach the problem at hand and a practical part about a sulphur feed system in case a decision is made to switch to burning fuels containing more chlorine.
The thesis also presents a cost estimate of the system and review of the environmental permit of the power plant.

The thesis was commissioned by Kerava Energy because they wanted to know whether peat could be removed from use and how boiler corrosion could be prevented in such a case.

2 Keravan Energia

Kerava Energy is a local energy company that produces district- and process heat, electricity, natural gas and consulting services. Whole Finland and Nordic countries form the market area where they sell electricity; district heat is produced locally for the city of Kerava, Sipoo and Karkkila and process heat for the nearby industrial area. The company has a number of power plants in the Kerava region, of which a few are basic load producing CHP plants and the rest are peak and balancing thermal power plants for the district heat network.

To reduce the environmental effects and streamline logistics of fuel transportation, the company has decided to build and operate a bioenergy power plant, where they combust locally produced wood chips and peat. (Figure 1.) Co-combustion of wood chips and peat produces much less dangerous emissions compared to coal combustion.

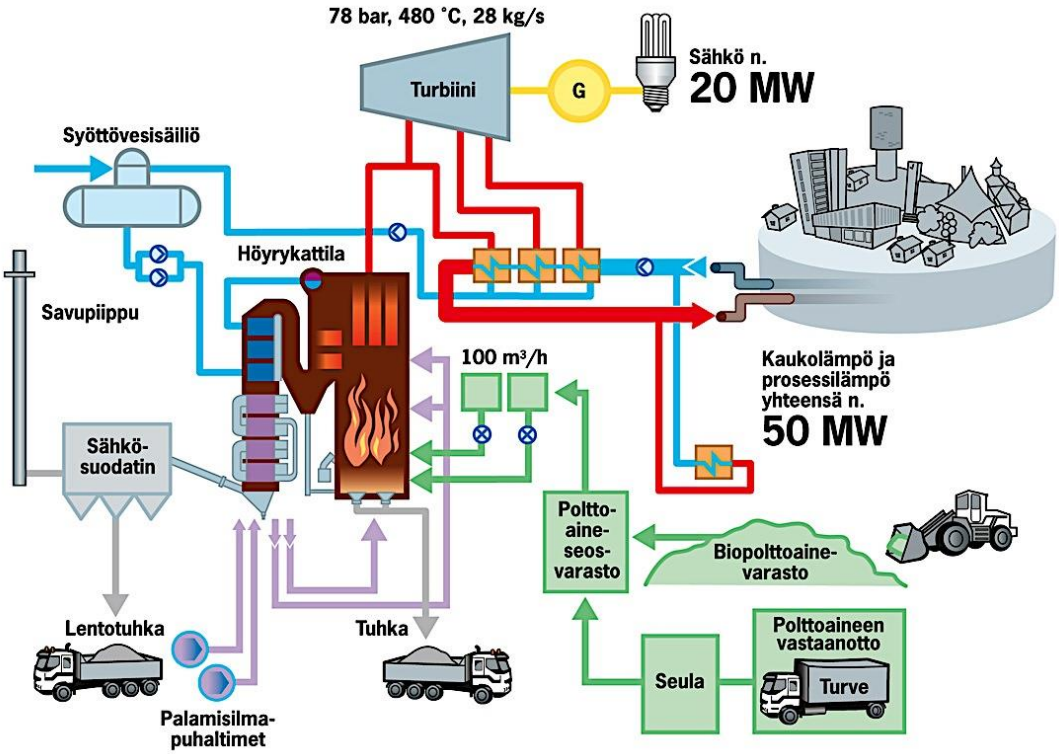

Figure 1. PI-chart of the power plant layout. [1]

3 Fuel qualities

The chemical construction of solid fuels is very complex. The chemical composition of biofuels is dependent on the plant species. [2. p, 128) Fuels contain naturally metals, which do not disappear, but can change their form according to changes in prevailing conditions. Such metals are for example alkali- and heavy metals. There are also naturally occurring heavy metals in the environment; they can be present in many different forms, such as minerals, water dissolved ions, gases, salts, bonded to organic or inorganic molecules or adsorbed onto particles. [3. p, 13] The chlorine concentration of the combustion gases depends on the chemical properties of the fuel and varies strongly according to fuel. During combustion nearly all of the chlorine contained in the fuel is volatilized and transformed into hydrogen chloride – gas. [4. p, 9]

Table 1. Common properties of typical fuels [4. s, 9]

Ominaisuus	Hake	Kuori	Puru	Jyrsinturve	Kivihiili
Kosteus, %	45-55	50-60	50-60	45-55	10
Tuhka, % (d)	0.5-2	1-3	0.5-1	6	14
Haihtuvat aineet, % (d)	80-90	70-80	70-80	65-70	30
Tehollinen lämpöarvo, MJ/kg (d)	19-20	19-20	19-20	20-21	29
Tehollinen lämpöarvo, MJ/kg (ar)	7-10	6-9	6-9	8-10	26
Hiili, % (d)	52	55	50	54	72
Vety, % (d)	6	6	6	5,5	4,5
Typpi, % (d)	<0,5	<0,5	<0,5	1,7	1,0
Rikki, % (d)	<0,05	<0,05	<0,05	0,2	<1,0
Happi, % (d)	40	37	43	33	8
Kloori, % (d)	<0,05	<0,05	<0,05	<0,05	<0,1

Table 2. Comparison of reed canary crass to other fuels [5. p, 107]

Analyysiparametrit	Ruokohelpi (Kevätkorjattu)	Ruokohelpi (Syyskorjattu)	Vehnän olki	Puupolttoaine	Palaturve
Tehollinen lämpöarvo k.a., MJ/kg	17,6	17,9	17,4	19,2	21,5
Tehollinen lämpöarvo saapumistilassa, MJ/kg	14,6	14,8	14,4	8,5	12
Kosteus,%	14	15	15	50	40
Haihtuvat aineet, %	74	72	73	80	70
Tuhkapitoisuus, %	5,5	6,5	7	1,5	4
Hiili, C, %	46	46	46	50	55
Vety, H, %	5,5	5,7	5,5	6	5,6
Typpi, N, %	0,9	1,3	0,5	0,3	1,5
Happi, O, %					
Rikki, S, %	0,1	0,17	0,15	0,05	0,25
Kloori, Cl, %	0,09	0,5	0,5	0,02	0,05
Kalium, K, %	0,2	0,8	0,8	0,2	0,05
Kalsium, Ca, %	0,2	0,4	0,4	0,3	0,5
Magnesium, Mg, %	0,05	0,2	0,1	0,05	0,05
Natrium, Na, %	0,01	0,01	0,1	0,01	0,01
Pii, Si, %	1,8	1,2	1,8	0,4	0,8
Tuhkan sulamispiste, °C	1404	1075	930	1150	1100
Arseeni, As, mg/kg kuiva-aineesta	0,2	0,1		0,1	2
Elohopea, Hg, mg/kg kuiva-aineesta	0,03	0,03	0,03	0,02	0,09
Kadmium, Cd, mg/kg kuiva-aineesta	0,06	0,04	0,05	0,1	0,1
Lyijy, Pb, mg/kg kuiva-aineesta	2	1	1	4	5

3.1 Qualities of peat

The decomposing process greatly alters the chemical construction of the plant matter. Peats are classified according to their botanical composition into different peat species. Taxonomically, peat species used for energy are called milled peat and sod peat of which milled peat is the preferred fuel as 90 % of the peat used for energy is milled peat. The average sulphur content for peat is approximately 0.24 % of dry weight. [6. p, 26 – 27]

The ash content of peat is approximately 3.8 % of dry weight, the sulphur content of ash is 0.14 weight %, and the chlorine content is 0.03 weight %. [7. p, 28]

Table 3. Chemical properties of peat [7, s. 29]

Kemialliset ominaisuudet	**Yksikkö**	**keskimäärin**	**vaihtelu**
Hiilipitoisuus, C	m-% k-a	54	51 - 59
Klooripitoisuus, Cl	m-% k-a	0,03	0,01 - 0,1
Fluoripitoisuus, F	m-% k-a	0,003	0,001 - 0,01
Kalsium, Ca	m-% k-a	0,4	0,04 - 2
Kalium, K (kok.)	m-% k-a	0,07	0,012 - 0,34
Kalium, K	m-% k-a	0,012	0,002 - 0,10
Fosfori, P	m-% k-a	0,05	0,005 - 0,28
Magnesium, Mg	m-% k-a	0,09	0,01 - 0,95
Rauta, Fe	m-% k-a	0,7	0,01 - 5,5
Pii, Si	m-% k-a	0,02	0,01 - 0,33
Natrium, Na	m-% k-a	0,06	0,002 - 0,31
Natrium, Na (etikkahappoliuk. pH3)	m-% k-a	0,003	0,0013 - 0,0075
Alumiini, Al	m-% k-a	0,2	0,01 - 2,2

3.2 Qualities of wood

Wood chips have many properties that make them environmentally friendly and relatively carbon neutral, depending on the utilization percentage but technically they are not completely problem free. Typically alkali metal and chlorine concentrations are low in woods, but they are easily released in gaseous form during combustion and thus are oxidized to oxides to form sulphates and chlorides. [8. s, 2]

The qualities of wood are affected by the species used, rate- and place of growth and age. Also fertilizing, storing, time of harvest and chemical and mechanical handling affect the properties of wood. In addition during spring harvest the wood is more nutritious and contains more minerals. [7, s. 18]

Table 4. Properties of selected biomasses.[9]

	Timber pellets	Timber chips	Saw dust	Bagasse briquette	Straw pellets	Peat	Recycled wood	RDF fluff
Moisture %	5-10	20-50	45-60	8	12	50	25	25
Lower Heating Value								
MJ/kg	17	7,5-13,9	6-10	16	14,7	9,3	14	13
Bulk Density kg/m3	650	130-280	300-350	650	650	340	300-400	100
Energy density								
MWh/m3	3	0,55	0,45-0,7	2,9	2,7	0,9	1,4	0,4
Ash % ds	0,9	0,4-5,3	0,4-0,5	6	7	5,1	5	10-20
S % ds	<0,1	<0,1	<0,05	<0,05	0,01-0,03	0,22	0,1	0,1-0,5
Cl % ds	<0,03	<0,05	<0,03	<0,03	0,1-0,8	0,02-0,06	0,1	0,3-1,2
Alkali % ds	0,1-0,3	0,1-0,3	0,1-0,3	0,4-0,7	0,3-1,7	0,1	0,1-0,5	0,4-1
P % ds	<0,05	<0,05	<0,04	<0,05	0,05-0,8	<0,35	<0,3	<0,5

4 Boiler corrosion

The majority of metals react to form oxides when they come in contact with oxygen. This is called oxidizing, in other words corrosion. In STP conditions, water is also needed for a metal to begin rust formation, either in the form of water or moisture from air, and it is much more corroding than just oxygen. The metal oxide layer which has been formed from the initial reaction between the metal and oxygen also acts as an inhibiting agent, thus slowing the further reaction rate or further oxidizing. In this case, the reaction speed is dependent on the ability of oxygen to diffuse through the metal oxide layer.

The corrosion areas of the flue gas area of the boiler are as follows:

- Firebox
- Superheaters, whose material corrosion is caused by temperatures exceeding the design limit

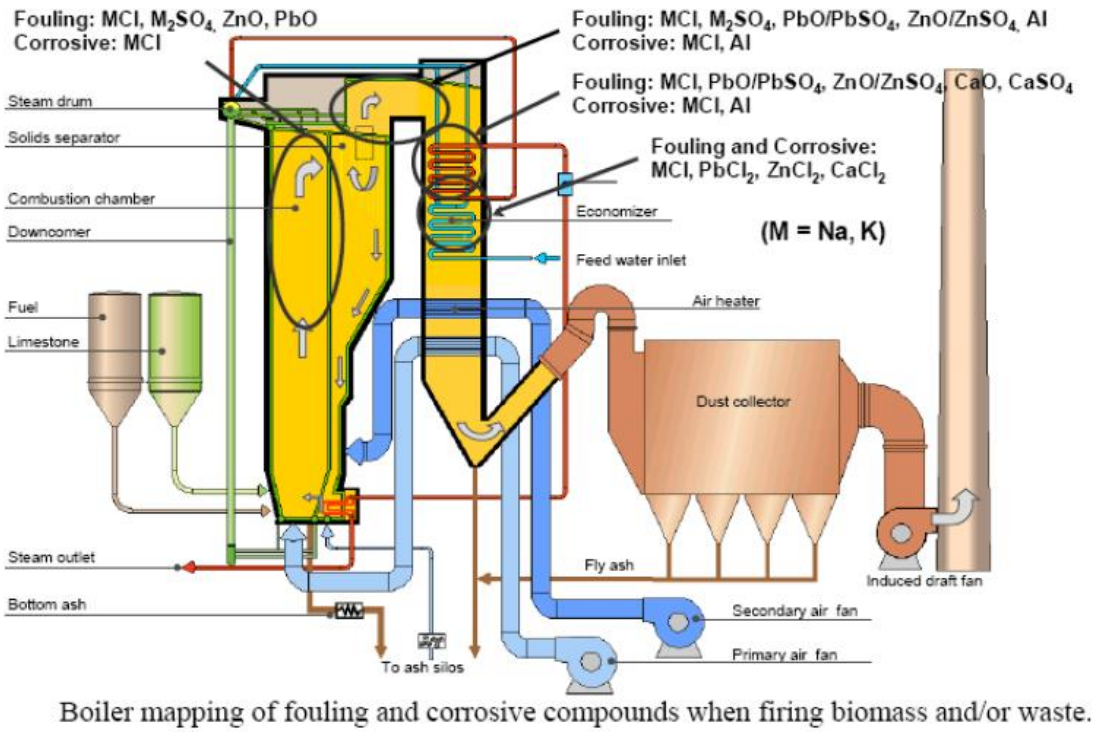

Figure 2. The corrosion spots at bubbling fluidized bed boiler [25. p, 29]

The corrosion-resisting properties of boiler metals is based on the phenomenon that a protective layer is formed on top of carbon and alloy steels. The denser and stronger the chemical bonds are between the oxides, the better corrosion protection the metal offers against corroding compounds and particles in the flue gas stream. Compounds or particles or any process that prevents the formation of a protective oxide layer or wears that layer off will hasten the corrosion of the metal surface. Soot blowers and fly ash in themselves are not corroding, but can remove or positively contribute to the removal of the protective film. In this case, the material behind the oxide layer becomes exposed to the hot flue gases, and the oxide layer is reformed if the environment where the metal exists permits it. The metal oxide layer is formed by converting the surface layer of the metal into its corresponding oxide form, thus losing a small quantity of the surface material. The puncture or complete failure of the material occurs when this cycle of metal conversion and subsequent loss and reformation of the oxide layer happens many times, causing a small loss of steel material in the superheaters. If the situation is not remedied in the super heaters for example, the thickness of the heater pipe materials wears so thin that they cannot endure the steam pressure inside them and a breakage will occur. The reason for this is the oxidation of a clean, unprotected metal. (7.)

The oxide layer does not completely prevent the oxidation in principle, but only slows it down. The physicochemical properties of the oxide layer and the environment, i.e. the flue gases and particles, are the determining factors which determine the corrosion speed. The corrosion which is found in the furnace and flue gas channel is usually caused or greatly accelerated by ash deposits formed on the pipe surfaces. The deposit in question causes a local environment susceptible to corrosion. [1. p, 284]

The material used in the superheaters is an important factor in the prevention and formation of corrosion. Commonly superheater pipes are an alloy of steel and some other metal. Superheater pipes in a BFB-boiler have to endure the effects of flying bed material, particles and the effects of erosion caused by ash and high-temperatures from the outside. And from the inside the strain is caused by highly pressurized, hot superheated steam within the pipe and especially in the bends. [3.]

Alkali metals are the primary route for chlorine transportation to super heaters. The sulphur found in the fuels reacts with the alkalis and shapes them so that chlorine cannot react with the alkali metals and is released as hydrogen chloride which is less cor-

roding. The co-combustion of fuels introduces chemical elements into the furnace which react together to form less corroding compounds. The corrosion rate is affected by the chlorine-to-sulphur ratio of the flue gases. [18. p, 22]

4.1 High-temperature corrosion

The corrosion caused by high-temperature conditions under oxidizing environment is called spalling, and it happens after the temperature is 600 °C and above. [1,2] Corrosion at high-temperatures is a mechanism of corrosion that especially happens in environments where corrosive components containing hot gases come into contact with susceptible surfaces, such as furnaces and engines. Fuels usually contain compounds such as sulphates which form compounds that have a low melting point; thus they melt into liquid salts at surfaces which are above the melting point of that said compound and are highly corrosive for steels and alloys normally relatively inert to corrosion and high-temperature.
Metals, such as iron, form different kind of metal oxide layers when they are exposed to oxygen and high-temperature. The layers formed by iron are as follows:

- Wüstite (FeO)
- Hematite (Fe_2O_3), red iron oxide
- Magnetite (Fe_3O_4), black iron oxide

Wüstite is only formed over temperatures of 570 °C. Its ion conductivity is high, and its ability to attach to the metal surface is poor. For this reason, iron oxidizes rapidly at high temperatures. Magnetite and hematite layers formed below this temperature are sufficient to protect against continuous oxidation.

Addition of chromium, nickel or molybdenum changes the qualities of the material so that a far superior protective film is created on top of the alloy. Alloying nickel with steel favours the formation of easily attaching magnetite + nickel oxide - film on top of the iron that enhances its corrosion resisting capabilities. Also increasing the chromium content decreases the corrosion rate. [10. p,137] Because chromium is more reactive, it reacts with the environment (flue gases) to form a protective oxide layer. When an alloy has more than 13 % or more chromium, the oxide layer is predominantly chromi-

um oxide and hence the metal is said to be fully passivated. If the metal has closures or deposits of sulphur or phosphorus, then in these spots the oxide film is not perfect. [10. p, 138]

With a proper alloy of steel and another metal the corrosion durability of superheater pipes can be greatly increased. The most common added metal to the alloy is chromium, to form ferrochrome. The chromium content of stainless steel is between 10 - 20 %, but in ferrochrome it can be between 40 - 70 %. The protective properties of chrome are based on the decreased ion conductivity on the surface because of the chromium oxide layer (Cr_2O_3). In highly alloyed chromium steels, chromium oxide is the predominant layer. Chromium oxide works well in the conditions exhibited in the furnace heat transfer areas. In very high-temperatures (> 1000 °C), aluminium oxide gives an exhibits a better protection against corrosion because chromium oxide starts to evaporate from the metal surface and the protective qualities are lost.

If the environment outside the metal contains other corrosion causing compounds than oxygen, the former reaction mechanisms are not plausible. Sulphur and oxygen rich environments affect the metal differently than just oxygen containing environments. In this kind of environment sulphur can diffuse through the protective oxide layer and form metal sulphides in favourable formation areas. The sulphide layer formed over fire tubes protects the tubes poorly against corrosion, unlike the oxide layer. Sulphide layer exhibits a tendency to spall and porosity and the sulphur found in the flue gases can lower the spalling temperature of metals by hundreds of degrees.

Inorganic molten compounds released from the combustion of fuels can under favourable conditions speed the oxidation reaction greatly when they condense to the surfaces. This is because in liquid phase ions can transport through the medium far faster compared to a solid phase. Especially problematic are alkali salts, such as sodium chloride. Sodium chloride (NaCl) forms sodium sulphate (Na_2SO_4) with gas phase sulphur, which when molten removes the protective oxide layer on top of the metal thus removing the protective film.

4.1.1 Chemistry of high-temperature corrosion

The formation of a galvanic cell occurs when there is a gas bubbling to an electrode that is in connection with its own ions. The following combinations can be prevalent: oxygen electrode in contact with a hydroxyl ion or chlorine in contact with a chloride-ion. If such ions are found in a solid medium and if the ions at hand have a high enough mobility in the solid, then it is a solid electrolyte, and the gas in contact with it forms half a cell from a galvanic cell. If the gas is an acceptor, as is oxygen or chlorine and it is in contact with a donor, such as metal or a solid electrolyte as an oxide, a galvanic cell is formed where oxygen uses the electrons donated by the metal to form oxides. [11. p, 156]

The reaction mechanisms of high-temperature corrosion are similar to that of aqueous based corrosion. In high-temperature corrosion, the diffusion of ions through the compact, dense solids is the rate controlling step. This is also true for other gaseous reactants such as sulphur and halogens.

The oxide layer is usually occurs as a film with a thickness of few millimetres. When the oxidation progresses, more oxide is formed and the thickness grows. However, after a certain thickness, the layer is peeled off from the metal; therefore all research in this area is aimed at cases where the corrosion product is present as a layer on top the corroding metal. [11. p, 157]

After the initial phase, when deposit is thick enough, for example a few tenths of millimetre or more, the growth of the deposit is controlled by the diffusion rate through the topmost layer. Growth in thickness increases the diffusion pathway, and the reaction rate decreases. This is only true if the corrosion product forms a thick, attached and compact layer on top the metal. According to Pilling and Bedworth [11.] when examining oxidation, inspecting volume ratios between the metal and the oxide will be important to study the reaction speed correlating with increases in oxide thickness. This ratio, called Pilling - Bedworth ratio can be expressed as follows:

P-B - ratio = volume of the oxide / the corresponding volume of the metal

If this ratio is not coherent, as is the case with alkali metals, the oxide will displace less volume than the metal so that cracks and pores will be present in the oxide through

which the reacting gas can freely act upon the metal; thus the oxide layer is non-protective. If the oxide layer has a large volume, such as tungsten, then the layer will have crevices and splinters because of compression stresses. In this case the oxide layer would not offer resistance against diffusion and would be non-protective. If the ratio is slightly higher than 1, the layer is dense, compact and offers the comparative protective properties.

The aforementioned case is true if presumed that the metal only forms one oxide and the bond between the metal and the oxide is strong. This presumption is not always true. The oxide layer can consist of two or more oxides, for example iron oxides, as mentioned in chapter 3.1. Also, the volume ratio can change according to temperature, since the expansion coefficients for metal and oxides are different. The expansion of the oxide can also create compression stress which can break the film. [11]

4.1.2 Catastrophic oxidation

In the case of alkali metals the oxide film does not protect the metal and oxidation continues unhindered. In this case the reaction is also exothermic, thus the temperature will grow. This increase in temperature will further accelerate the oxidation reaction and hence a positive feedback - loop occurs, and when this happens it is said to be catastrophic. Catastrophic oxidation refers to oxidation products which create a liquid film over the metal which is easily removed, exposing new fresh metal to further oxidation. In the case of tungsten, vanadium and molybdenum these oxides have a lower melting point than the metal itself, thus no protective oxide layer is formed. Catastrophic oxidation is especially the problem when combusting fossil fuels such as coal or oil products which have vanadium. [10. p, 158-159]

4.1.3 High-temperature corrosion in other environments

High-temperature corrosion causes metal degeneration in other environments also when there is nitrogen, halides and sulphur and its oxides together or separated. The severity of corrosion grows when the material is exposed to an environment, where there is two or more corrosive gases. Commonly the protective properties of the oxide

film are based on their good ability to attach to the metal, compactness and high melting point. In other environments the formation of salts, such as chlorides and sulphates because of sulphur or chlorine presence from fuels. Such products have significantly lower melting points than corresponding oxides. Thus the corrosion product forms a molten film over metal surface which drains exposing new fresh surface to the corrosive gases. Formation of liquid corrosion products is especially dangerous, because it causes unevenness accompanied by the catastrophic loss of metal. [10. p, 171]

4.2 Low-temperature corrosion

Low-temperature corrosion is by definition corrosion which happens below temperatures of 600 °C. [2.] The best examples of this are hydrochloric acid and sulphuric acid corrosion which happens below their corresponding acid dew points. Fuels which release chlorine have a tendency to form hydrochloric acid, since hydrogen is prevalent in all combustible materials and correspondingly fuels containing high amounts of sulphur will create highly corrosive reaction products which under favourable conditions will react to form ill wanted compounds. Because of the high-temperature during combustion, the chlorine and sulphur are released and they react with corresponding elements found within the furnace to produce acids. Chlorine reacts with hydrogen to produce hydrochloric acid and sulphur reacts with excess oxygen from the primary feed air to form mainly sulphur dioxide (SO_2), but also sulphuric trioxide (SO_3). There is always some moisture in the flue gases and the furnace which comes from feed air and the fuel, unless pure oxygen is used. When the dew point of the flue gases is achieved, the moisture is condensed and together with sulphur trioxide form sulphuric acid (H_2SO_4) and corroding films. The same is also true for chlorine, as the chlorine first reacts with hydrogen to form hydrogen chlorine (HCl) which then reacts with water vapour to form hydrochloric acid (HCl). [9. p, 196]

The amount of for example sulphur trioxide depends on the following:

- Sulphur content of the fuel
- Retention time of flue gases in the furnace
- Temperature of furnace and walls
- Excess oxygen
- Amount of catalysts

The corresponding pathways also hold true for chlorine, except oxygen does not have a role in chloride generation, but alkali metals.

Sulphuric acid and hydrochloric acid corrosion is prevalent in areas of the power plant where flue gas temperature is low, that is after superheaters and economiser when all the available remaining heat energy has been extracted from the flue gases. Commonly low-temperature corrosion occurs on air preheaters and stack at surfaces where the temperature goes below 200 °C. The acid dew point temperature is usually approximately 150 °C, and when the flue gases cool down below this temperature, the acid droplets start to condensate on the aforementioned surfaces. If the temperature keeps on decreasing, below 50 °C, water dew point is breached and sulphurous acid is formed which corrodes steel even more strongly than sulphuric acid.

Steel corrodes at atmospheric conditions when the relative humidity is 75 % or more. It is said, that when relative humidity is 75 % or more, a film with a thickness of three water molecules is formed of the metal surface. This acts already as the steel or iron is immersed in water. For copper or nickel, the relative humidity is 85 % or 100 %. Iron is more susceptible to compounds which concentrate from normal atmosphere. Even though no oxygen would be available for depolarization, the ferritic ion in the system acts like an acceptor forming ferric ions. [10. p, 135]

It is estimated that 1 - 5 % of the sulphur dioxide of the flue gases further reacts to form sulphuric trioxide, according to which the flue gases from peat combustion has an SO_3 - concentration of 1 - 5 ppm and wood having below 1 ppm. The flue gas humidity when burning peat, and wood chips is 15 - 25 volume percent and pellets 10 %. When combusting peat the sulphuric acid dew point are 120 - 140 °C, wood chips maximum 125 °C and pellets 115 °C. When co-combusting wood and peat, the dew point is difficult to estimate calculatedly because the SO_3 reacts with the alkali metals from wood ash. [11. p, 19]

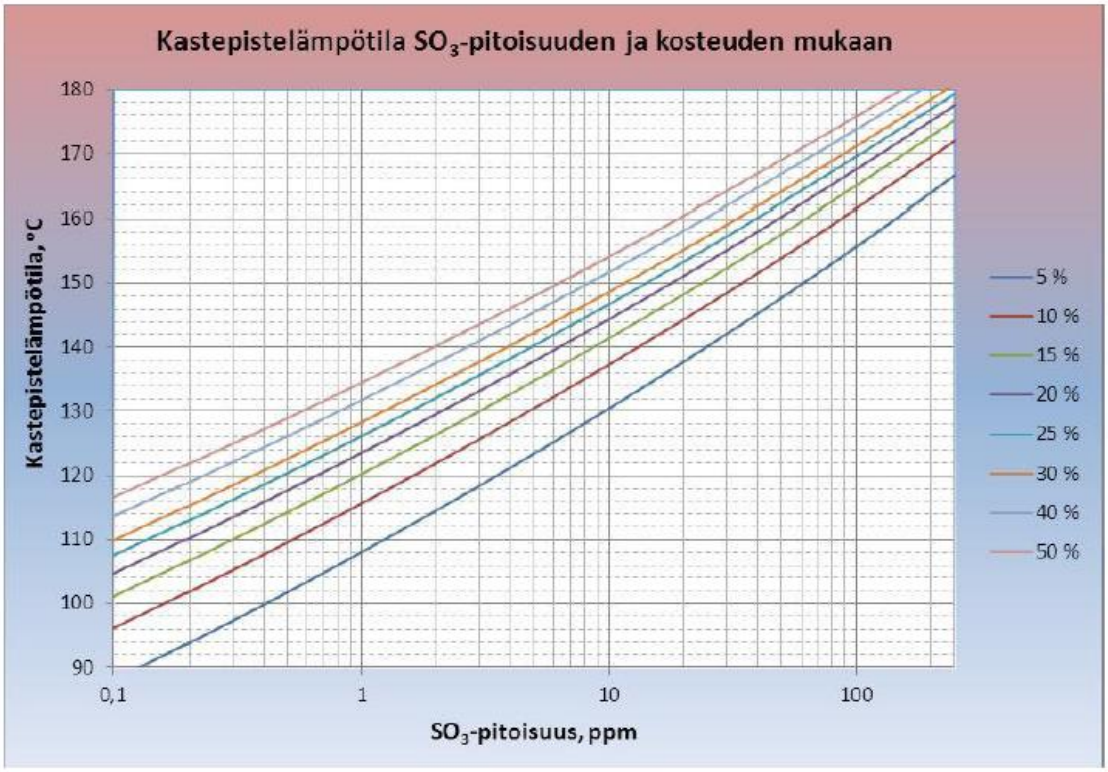

Figure 3. The acid dew point of sulphuric acid in the flue gases, according to the SO_3 - concentration and vapour percentage. [11. p, 20]

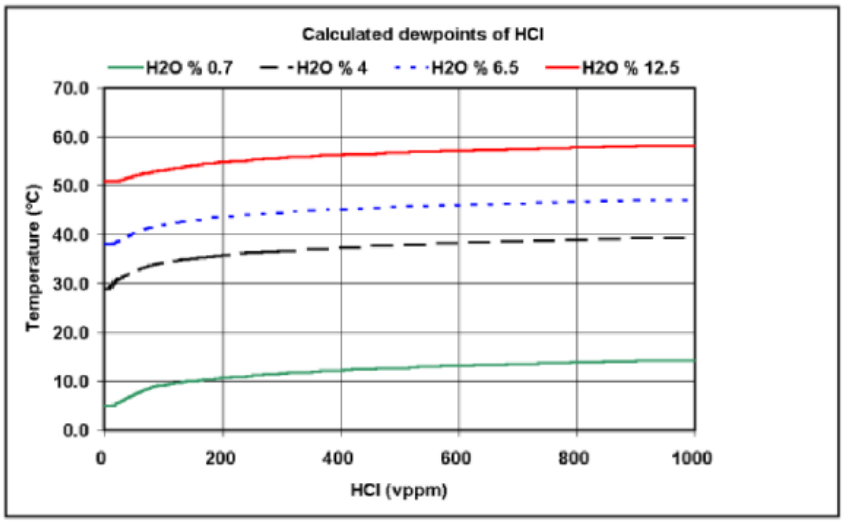

Figure 4. The acid dew point of hydrochloric acid: dependence on the humidity and concentration of hydrogen chloride. [22. p, 65]

4.3 Erosion corrosion

This type of corrosion is seen when the metal is in contact with a fast flowing phase, liquid or gas, and metal erosion is increased because of the corroding effect of the phase. The wear of the metal is not only because of the electrochemical activity but also because of mechanical actions. Common features of erosion corrosion is the formation of grooves, holes, waves and wells to the surface of the metal. The attack forms sharp edges and the corrosion is usually in line with the phase flow. [10. p,110] Small and very hard particles in the flue gas stream cause wear to the surfaces when striking materials. Peat encompasses high amounts of wearing quarts compounds which create wearing particles.

Erosion corrosion can also happen in a gas media, for example a flue gas stream. In this case, the corrosion product is usually in the form of a protective layer on top the metal. In certain spots, this layer is brittle and mechanically weak. If the gases have a high flow velocity, this film is easily peeled off and new metal surface is revealed for new corrosion attack. As mentioned in chapter 3, the corrosion product off ill wanted form, it is continually peeled off from these places and then more erosion and corrosion occurs. For example, a magnetite layer does not offer protection against erosion corrosion because of bad attraction. Metal oxide layer offers better protection against erosion corrosion than sulphite, sulphate or chloride-layer. Oxides are harder than other compounds of the same metal. [10. p, 113]

4.4 Chlorine

Chlorine is a gas from the halogen group and in STP-conditions is in the form a diatomic gas. (Cl_2). As a free atom it is poisonous to humans and strongly corrosive. It is a halogen that forms salts and nearly all of the chlorine found in earth's crust is in the forms ions. For this, reason a large part of the solid chlorine is found bound to alkali metals in the form of chlorides because it easily bonds with nearly all chemical elements and occurs as chlorides. In these compounds it is found as chloride-ions (CL^-).

The oxidation number for the solid- and ion forms of chlorine is -1. Then they are present as ionic chlorides, organo chlorides and hydrochloric acid. Because chlorine is not

a gas under STP conditions but usually bound to, for example, sodium which is an alkali metal. During combustion, these different elements or minerals are vaporized or can react to form a molecule and thus form compounds that further corrode and react with other metals and compounds to harm power plant components.

In coal, chlorine is found in the following forms:

- Inorganic chlorides
- Organo chlorides
- Chloride-ions in saltwater and other humidity in the coal

Spectroscopy has shown that a large fraction of the American coal, chlorine is prevalent as CL^- ions in the humidity adsorbed onto micro cracks and spores. In other cases occurs in the form of crystallized NaCl which has precipitated from chlorine-rich solution when the coal has been dried. [2. p, 774]

One corrosion mechanism is also when the chlorides are released as HCL that is hydrogen chloride during the combustion process. Hydrogen chloride reacts with water to form hydrochloric acid. Hydrogen chloride itself is also corrosive and act as corrosive agent even in the absence of water.

If the temperature at the superheater or reheater area is approximately 600 - 650 degrees, HCl contributes the release of sodium and potassium from coal ash. They react with gaseous sulphur to form sulphates. Sodium- and potassium-sulphates cling to cooler surfaces further down the flue gas duct. The outermost layer of this sulphate deposit can become so hot that a high SO_3 partial pressure can occur which leads to a molten alkali-sulphate layer on top of the metal. This molten alkali-sulphate mass is highly corrosive; thus hydrogen chloride causes indirect damage, but it is directly related to chloride-concentration. [2. p, 775]

4.4.1 Alkali metals

The alkali chlorides in the ash deposit covering the superheater pipes can sulphate by reacting with the SO_2 or SO_3 - molecules to form gaseous chloride compounds, such as HCL or chlorine gas. [12. p, 74]

In the case of potassium chloride the reactions can be given as follows: *[12., p, 74]*

$$2KCL(s) + SO2(g) + (½)O2(g) + H20(g) \rightarrow K2SO4(s) + 2\,HCl(g)\ and$$
$$2KCl(s) + SO2(g) + O2(g) \rightarrow K2SO4(s) + Cl2(g)$$

In addition to sulphating chlorine compounds, can also be formed from the reactions between alkali chlorides deposited in the ash layer and the reaction product layer found from the surface of the metal. In the case of sodium chloride, the reactions can be written as follows:

$$2NaCl(s,l) + (½)Cr2O3(s) + \left(\frac{5}{4}\right)O2(g) \rightarrow Na2CrO4(s,l) + Cl2(g)$$
$$2NaCl(s,l) + Fe2O3(s) + (½)O2(g) \rightarrow Na2Fe2O4(s,l) + Cl2(g)$$

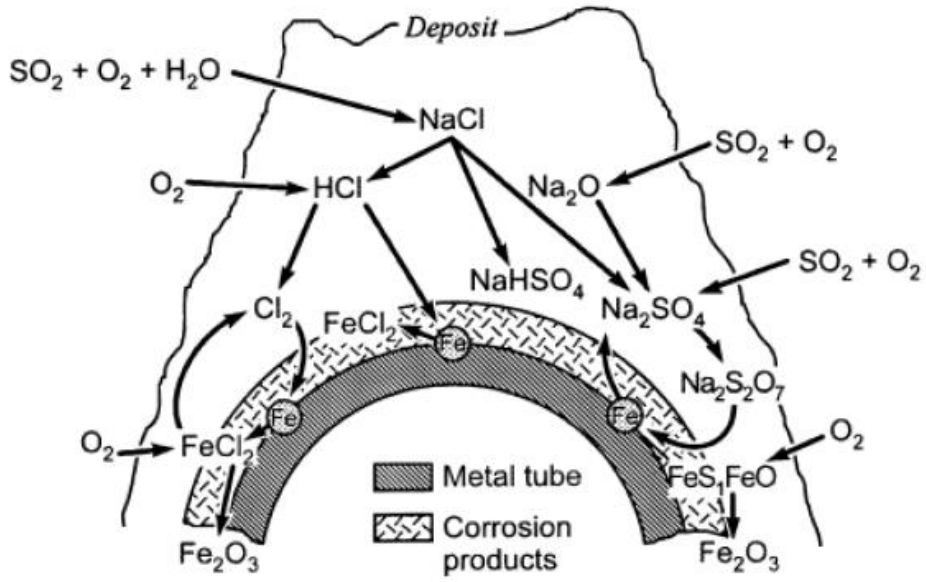

Figure 5. The reactions and mechanisms of the alkali chlorides on the surface ash deposit of a superheater pipe. [12. p, 75]

4.5 Chlorine corrosion

Alkali- and earth-alkali metals such as sodium react with sulphur to form a sulphate mixture, which have an initial melting temperature is 650 C°. If the proportion of these sulphates in the ash is large, then the furnace is also subjected to fouling. If the fuel also includes chlorine, then the situation declines rapidly. If the flue gases contain a combination of sodium, potassium and their sulphate and chloride mixtures, the lowest possible melting point of the ash might be as low as 515 C°. The superheater surfaces are usually at such temperatures; consequently, the ash is likely to melt resulting in severe corrosion damage because the partially molten mixture of alkali sulphates and chlorides is very corrosive. [13. p, 286]

When the temperature is over 900 C°, this type of chlorine corrosion does not occur in practice, but at lower temperatures considerable chlorine attacks are known to occur at the protective oxide layer. Also at very low temperatures, that is below 80 degrees, hydrogen chloride vapour reacts with water vapour to produce liquid acidic condensate and hydrochloric acid is formed because of chlorine. [2. p, 775]

From the perspective of heat surface slagging, fouling and high-temperature corrosion, especially problematic are alkalis, such as potassium and sodium, which are present in fuels containing plant-based green matter. Chlorine is usually found as sodium chloride. Spruce contains higher concentrations of alkalis and chlorine than pine. These alkalis contribute to the transportation of chlorine to superheater surfaces, and one the remediation methods is to co-combust peat and wood chips where peat contains sulphur. The sulphur reacts with the alkali metals in a way that the chlorine is released into the flue gas stream as hydrogen chloride and thus does not form alkali chlorides. Alkali sulphates and hydrogen chloride are not severely corroding in fluidized bed combustion. The fouling and corrosion of the boiler is affected by the sulphur - chlorine ratio of the fuel. If the sulphur - chlorine ratio of the superheater area flue gases is over 2, then slagging and fouling decreases, and if it is over 4, the decrease is considerable.

Wood contains very little sulphur; thus the sulphur content of the flue gases from wood combustion is low. This leads to alkali metals forming alkali chlorides, which easily melt at low temperatures into molten salts. Chloride salts are formed into sticky layers on top the heat transfer surfaces increasing the risk of high-temperature corrosion. The addition of peat into the combustion process increases the sulphur content so that the

alkali metals bind with sulphur forming sulphates and the released chlorine bonds with hydrogen to form gaseous hydrogen chloride (HCl). Hydrogen chloride is transported with the flue gases out of the boiler and does not cause considerable chlorine corrosion or chlorine release risk. Co-firing achieves noticeable benefits in the control of emissions and fouling, thus the usability of the boiler facility increases. [14. p, 3]

The metal being weakened chlorine and sulphur react with it to form reaction products which do not protect it. The released chlorine from the layer reacts with the pipe material and when oxidized forms hydrochloric acid or free chlorine which can repeatedly react with the pipe material. [15. p, 29]

During the combustion of biomass the released alkali metals can form alkali chlorides (KCl and NaCl) with the chlorine released during the process to condensate on the heat transfer surfaces. In pulverized coal-fired boilers the superheater surfaces are most prone to fouling and corrosion because there is the greatest temperature difference between the flue gases and surfaces. [12. p, 12]

The combustion process evaporates the alkali metals as gases which condensate as sulphates and chlorides into the fly ash particles, thus lowering the melting point which leads to the adhesion of fly ash on to the surfaces. The chlorine content of biomass plays an important role in this because as easily vaporizing components they increase the chlorine amount that easily condensates on to the fly ash. [12. p, 68]

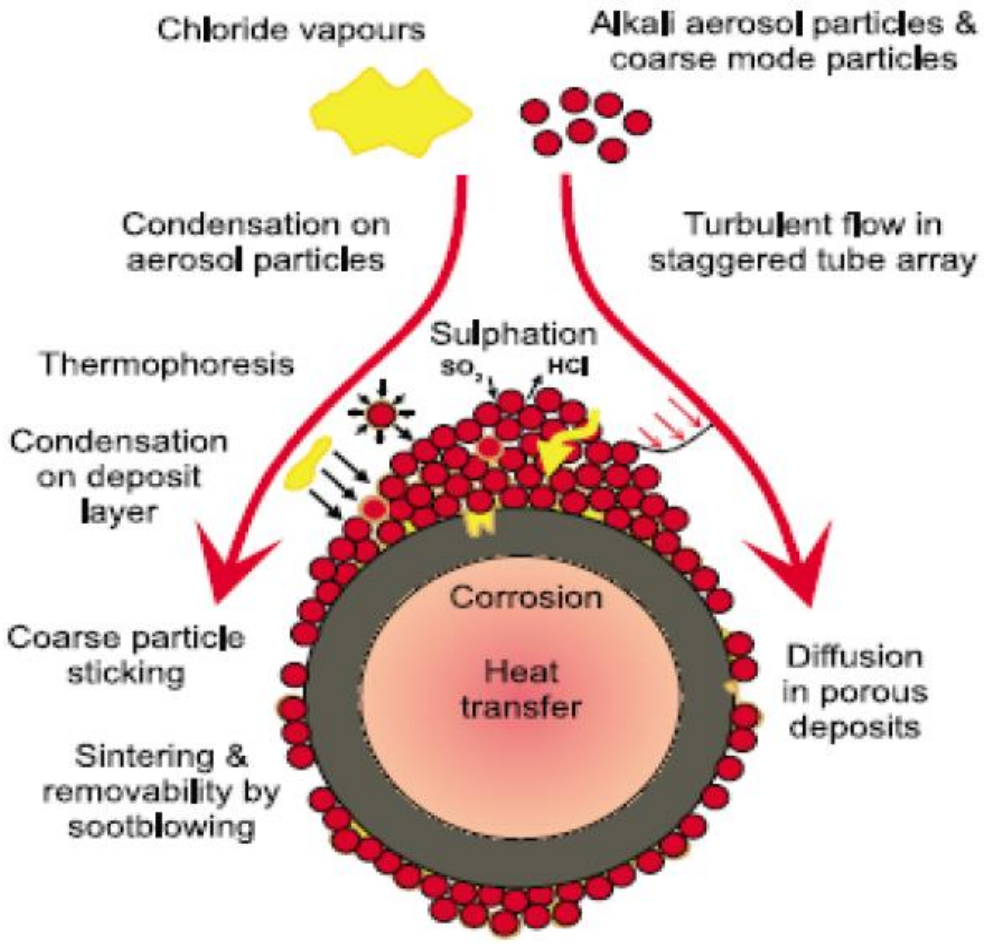

Figure 6. The formation of the ash layer [12. p, 69]

The following corrosion mechanisms are possible under the conditions presented by co-combustion:

- Processes where there occurs a reaction between metal or metal oxide and gaseous chlorine compounds, for example chlorine gas and HCl
- Processes where there occur solid phase reactions with alkali chlorides, such as KCl and NaCl
- Reactions with molten alkali metals and other chlorides [12. p, 71]

The areas most prone to high-temperature chlorine corrosion are those heat transfer surfaces to which an ash deposit with alkali chlorides is formed in combination with

high enough material temperatures. This is most affected by the chemical composition of the fuel and the temperatures of the material surfaces. In co-combustion the sulphur and chlorine content has a great significance with regards to the appearance of corrosion. It has also been shown that high-temperature chlorine corrosion requires that material has exceeded a threshold temperature value, which has been shown for material to be 450 °C. [12. p, 76-77]

The sulphur included in the fuel has great significance when the corrosion caused chlorine happens or not. In addition to sulphur, naturally the chlorine content also has high significance whether chlorine corrosion occurs or not.

The deposit of alkali chlorides on to the convection part of the boiler's superheater area affects strongly the corrosion rate. Temperature is crucial in this deposition, and only in a certain temperature range can alkali chlorides be sulphated before they enter to the convection part. The sulphating reactions at hand are only possible when the flue gas temperature is between 800 – 950 °C. If the temperature is higher or lower, sulphating does not occur, and the alkali chlorides enter the convection area of the boiler.

When combusting waste, fuels chlorine and alkalis of the ash form alkali chloride salts and their corresponding melting temperatures are as follows: [16. p, 31]

- NaCl - 801 °C
- KCl - 801 °C
- HCl - 771 °C

As shown in the following chapter, the alkali chlorides can appear in two different forms in the flue gases: either molten or vaporized form. When the alkali chloride vapor encounters the superheater surface, it condensates and sticks to the surface. The protecting oxide layer is broken when the molten salt attaches to the pipe and corrosion begins. The corrosion caused by chlorine is usually spot corrosion. [16. p, 31]

4.5.1 Effects of gas phase chlorine compounds on corrosion

The chlorine compounds that are in gas phase enhance the corrosion of heat transfer surfaces. As mentioned in the previous chapter, the most common gaseous chlorine compounds are HCl and Cl – gas. These gases cause different gas phase corrosion reactions and affect the steel with different high-temperature corrosion mechanisms. The reactions differ according to whether reducing or oxidizing conditions prevail at that particular spot or environment. When the steel is exposed to oxidation and oxide film has been developed, it is commonly sufficiently steady and dense that it offers protection against continuing oxidation. Chlorine has an ability to penetrate the protecting film and continue the corrosion reactions, and this is how superheater corrosion is caused by gaseous chlorine compounds. This is called active oxidation, which has been mentioned in chapter 4.1.2 [12. p, 71]

4.5.2 Effects of solid phase chlorine compounds on corrosion

During co-firing the heat transfer surfaces of the boiler on the flue gas side might accumulate an ash deposit which contains relatively large quantities of different alkali chlorides. These chlorides might cause a rapid increase in the corrosion reaction on the heat surfaces and the chlorides at hand might highly influence the corrosion caused by the ash deposit. The chlorides in the ash deposit might affect with two different mechanisms:

- The chlorine compounds in the ash deposit with high partial pressure near the metal surface can cause corrosion with the same principles as gaseous chlorine compounds. Similarly gaseous chlorine compounds can be formed when alkali chlorides sulphate or when the alkali chlorides in the deposit influence reactions between the reaction product layers formed on top the metal alloy.
- The chlorides in the ash deposit may form eutectic mixtures, and these dissolve the oxide film protecting the metal

4.5.3 The effects of molten phase or eutectic mixtures on the corrosion speed

One of the mechanisms is related to easily melting eutectic mixtures. The alkali chlorides in the ash deposit form eutectic mixtures with many different substances. The possible molten phases accelerate corrosion speed significantly. This occurs primarily because of two reasons:

- The rate of chemical reactions increases when substances are in a liquid phase
- Liquid phase offers an electrolyte or route for ion transportation for electrochemical reactions [12. p, 75]

Potassium chloride can form eutectic mixtures with iron and chromium [12. p, 75]

Table 5. Melting and eutectic temperatures of different substances [12. p, 76]

System	Melting/eutectic temperature (°C)	Composition at the eutectic point (mole % alkali)
NaCl	801	–
KCl	772	–
$FeCl_2$	677	–
$CrCl_2$	845	–
NaCl–$FeCl_2$	370–374	c. 56
KCl–$FeCl_2$	340–393	45.8–91.8
NaCl–$CrCl_2$	437	53.7
KCl–$CrCl_2$	462–457	36–70

Specifically systems formed of NaCL-$FeCl_2$ and KCl- $FeCl_2$ are eutectic mixtures, which, when present in the ash deposit, strongly accelerate the corrosion rate.

4.5.4 Active oxidation

As shown in chapter 4.1 metals corrode at high-temperatures without a liquid electrolyte. [17. p, 3] Active oxidation occurs when metal temperature is over 450 °C and it comprises many steps.

1. Oxidation of hydrogen chloride with water vapour in gas or chlorides, for example NaCl reacting with metal oxides to form chloride gas on tube surfaces:

$$2HCl + 0{,}5\ O2 \rightarrow Cl2 + H20$$
$$2NaCl(g) + Fe2O3 + 0{,}5\ O2 \rightarrow Na2Fe2O4 + Cl2$$

2. Intrusion of chlorine through the metal oxide layer into the oxide - metal boundary layer and reaction with iron or other metal component in the pipe, thus forming metal chlorides:

$$Fe + Cl2 \rightarrow FeCl2(s)$$
$$Fe + 2HCl \rightarrow FCl2(s) + H2(g)$$

3. Diffusion of metal oxide vapours outwards from the oxide layer covering the pipes and the reaction of that steam vapour with the excess oxygen of the flue gases, forming more metal oxide and chlorine:

$$FeCl2(s) \rightarrow FeCl(g)$$
$$3FeCl2 + 2O2 \rightarrow Fe3O4 + 3Cl2$$
$$2FeCk + 1{,}5\ O2 \rightarrow Fe2O3 + 2Cl2$$

In step 3 of active oxidation, the chlorine is released and it diffuses into the bulk gas which is the flue gases. However, some of the released chlorine can diffuse back into the metal / oxide – boundary layer and reacts with the metal to form volatile metal chlorides. Thus, a cycle is formed where continuous transportation of metal in the form of a chloride is transported away from the surface towards the higher partial pressure of oxygen. [17. p, 3]

Here are a few reaction equations:

$$M(s) + Cl2(g) \rightarrow MCl2(s)$$
$$M(s) + 2HCl(g) \rightarrow MCl2(g) + H2(g)$$

where M is some of the metal of the alloy mixture. In the reaction, the formed metal chlorides have a high steam pressure at the boundary layer of the film, thus continuous metal chloride evaporation can occur. [12. p, 72]

Vaporized metal chloride diffuses to the oxide film surface and reacts with flue gases to form chlorine gas again. The oxidation of metal chloride can be given by the following equations:

$$3MCl2(g) + 2O2(g) \rightarrow M3O4(s) + 3Cl2(g)$$
$$2MCl2(g) + \left(\frac{3}{2}\right)O2(g) \rightarrow M2O3(s) + 2Cl2(g)$$

The released chlorine gas can perform another cycle, that is to diffuse to the metal surface, and the corrosion reaction continues according to the initial reaction equation.

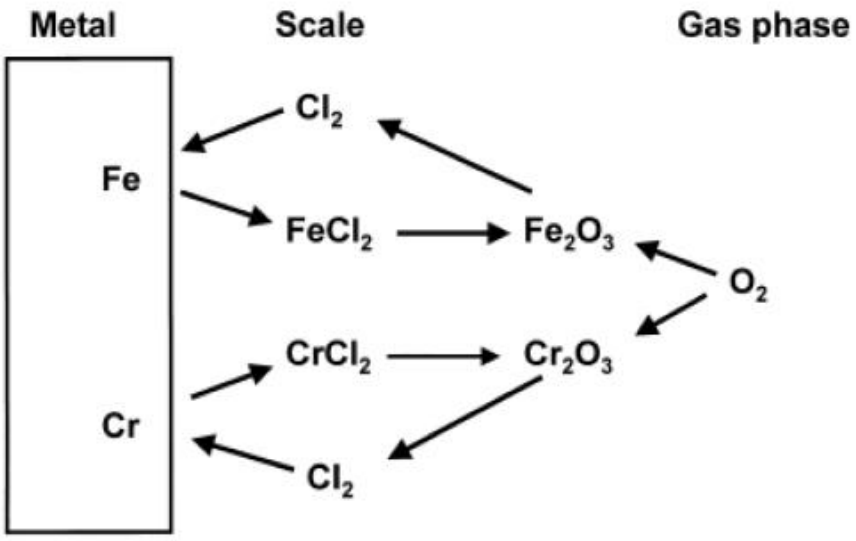

Figure 7. Corrosion mechanism caused by chlorine. [12. p, 72]

As stated in section 4.5.3, under reducing conditions the cycle in Figure 5 is possible. Reducing conditions cause that a protective oxide film cannot be formed on to the surface of the metal and chlorides are formed directly onto the metal without diffusing. Otherwise the mechanism is same as in oxidative environments. [12. p, 73]

4.5.5 Reducing environments and corrosion

Local reducing conditions can cause damage to the oxide layer protecting the metal and hence hasten the formation of corrosion damage. If there exists, in addition to the aforementioned conditions, chlorine or sulphur compounds, like different sulphides or chlorides, then corrosion formation worsens considerably. [13. p, 284] When the oxide layer is sufficiently weakened because of the reducing conditions, sulphur and chlorine react with the exposed metal and the formed reaction products, chlorides and sulphides will not create a proper corrosion protection for the metal.

The slagging of metal surfaces corrodes remarkably fast if the deposit is molten at the surface temperature of the metal. Very problematic are the alkali sulphate – chloride – mixtures.

In reducing environments HCl diffuses through the protecting metal oxide layer to the base metal to form volatile iron chlorides. This kind of an attack creates grain boundary corrosion that causes fractures and prevents the spalling of the oxide layer. The HCl – attack under reducing conditions generally occurs at the evaporating pipes. [2. p, 775]

4.5.6 Sulphur – chlorine ratio

As said shortly in section 4.1, the corrosion potential of a boiler can be evaluated by the molar ratio of sulphur and chlorine (*S* / *CL*)

$$\frac{S}{Cl} = \frac{S/M_s}{Cl/M_{cl}},$$

S is the amount of sulphur, *CL* is the amount of chlorine, and Ms and Mcl are the molar masses of the chemical elements.

- If the molar ratio is less than 2, then corrosion is highly likely with this fuel
- If the ratio is between 2 and 4, then corrosion is opportunistic, meaning it depends on the boiler design and the parameters of combustion
- If the ratio is over 4, then corrosion prevalence is highly unlikely (Salmenoja 2000)

4.6 Prevention of corrosion

It is possible to add elemental sulphur or ammonium sulphate ($NH_4 2SO_4$) into chlorine containing fuels. [7. p, 22]

Low-temperature corrosion can be prevented by the following measures:

- Keeping the flue gas temperature high enough
- Decreasing the amount of air during combustion, less excess oxygen which could react with sulphur
- Neutralising sulphur compounds by feeding magnesium compounds
- Feeding ammonium into the flue gas channel [9. p, 197]

Chlorine corrosion is mainly prevented by the following methods:

- Highly alloyed superheater materials
- Prevention of chlorine transportation from the furnace onto the superheater surfaces
- Superheater configuration

It should also be made sure that there is a proper sulphur-to-chlorine ratio as mentioned in chapter 4.5.6 so that the alkali - chloride formation is prevented. In addition, it should be ensured that eutectic mixtures are not formed, thus managing the correct temperature of the flue gases and superheater material temperatures.

4.6.1 Protection methods

Many metals need to be protected from oxidation since they naturally have insufficient qualities against high-temperature corrosion by themselves. It is also necessary to lengthen the life span of the component, especially if very wearing media such as flue gases or highly corrosive compounds affect the component at hand. Since the oxidation mechanism is based on diffusion of particles through the protective layer, it is important that the coating has such properties which prevent the diffusion process and offer high ability to attach to the substrate metal.

The most important quality of course is high melting- and boiling point. As mentioned before, high resistance against oxygen diffusivity and very little spot defects are highly wanted qualities. The coefficient of the coating thermal expansion needs to be comparative to the substrate metal, and the possible materials preferably need to be regenerating. [10. p, 172]

Silicon, aluminium and chromium are elements, and especially their oxides, nitrides and borides offer the aforementioned desired qualities. There are many methods how to spread the coating on to the metal surface. It has been shown that for high-temperature applications, [10. p, 172] external application is not suitable because it does not provide the desired properties. The bond between the substrate is mechanically weak and non-regenerating. The best method is diffusion coating, where the coating material, such as silicon, aluminium, boron or nitrogen is impregnated with atoms that develop into the substrate metal. The depth of penetration depends on the time and temperature. The surface is enriched with these elements and forms corresponding compounds, such as silicates, aluminates, borides and nitrides. When exposed to an environment, these elements are selectively oxidized and create the protecting film. It has been proven that a multilayer protective coating naturally offers more protection than singular coating.

Vattenfall is developing a method called ChlorOut, where ammonium sulphate disintegrates sulphur trioxide when it is injected into the furnace to approximately 800 – 900 ° C temperature. Sulphur reacts with potassium chloride (KCl) to form less harmful potassium sulphate (K_2SO_4) and easily vaporized chlorine containing gases. (Cl2 or HCl). In this case, alkali chlorides are condensed less into the superheaters and corrosion occurrence decreases. (18, 22)

4.7 Material choices

The desired qualities for the material for high-temperature applications has already been discussed in chapter 4.6. Highly alloyed steels with molybdenum and chromium offer desired properties.

5 Sulphur feed system

One of the aims of this thesis was to study the effects of chlorine corrosion if peat would be removed from the co-combustion process. It was studied whether the removal of the sulphur source would increase the alkali chloride amount in the combustion process, and if that proved to be the case, an alternative source of sulphur would need to be presented to remediate the situation by creating desirable reaction products to prevent the corrosive chloride formation.

As the chloride creating would be prevented with the introduction of a sulphur source, the following sulphur feed system is recommended:

- Storage silo outside the power plant
- Mechanical transfer of sulphur from the storage silo in to the feed silo near the boiler, pneumatically operated
- Compressor to create compressed air
- Pipeline from the storage silo into the feed silo
- Dust remover
- Feed silo inside the boiler house
- Screw feeder
- Dispenser
- Analyser for the dispenser which is based on the flue gas sulphur concentration

Sulphur is supplied in as big bags and it in the form of small granules. It is pneumatically moved from the outdoor silo to the indoor one. [18.] Pneumatic drive either by overpressure blowers or with vacuum which is created with the compressor. The feed silo is placed at the side of the boiler near the fuel feed. From here the sulphur powder is dispensed with the screw feeder, which is controlled according to stoichiometric data received from the sulphur dioxide analyser. [19.]

Sulphur can be either directly purchased from Tamro or corresponding chemical supplier; alternatively, it is also possible to utilize sulphur which has been created as a side product from many industrial processes, such as coal burning in power plants. Utilizing or mitigating the creation of industrial waste streams is in line with sustainable development and the increase of general efficiency; hence the sulphur generated at the flue-

gas sulphur removal process is recommendable, if a suitable technical implementation is available. Appendix 1: Material safety data sheet for sulphur.

5.1 Raumaster – sulphur feed system

A schematic of the Raumaster sulphur feed system in figure 8.

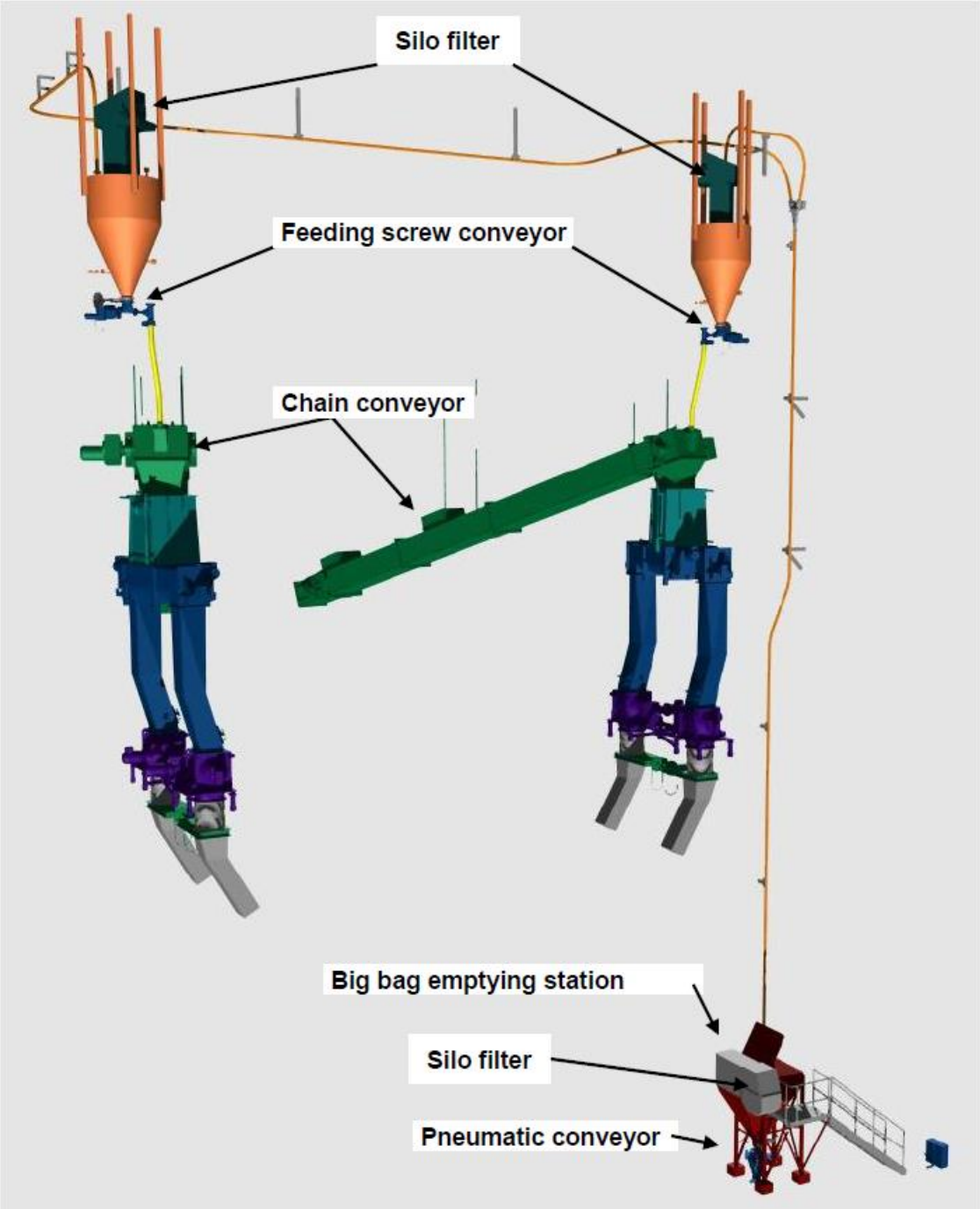

Figure 8. An exemplary Figure of the system. [20.]

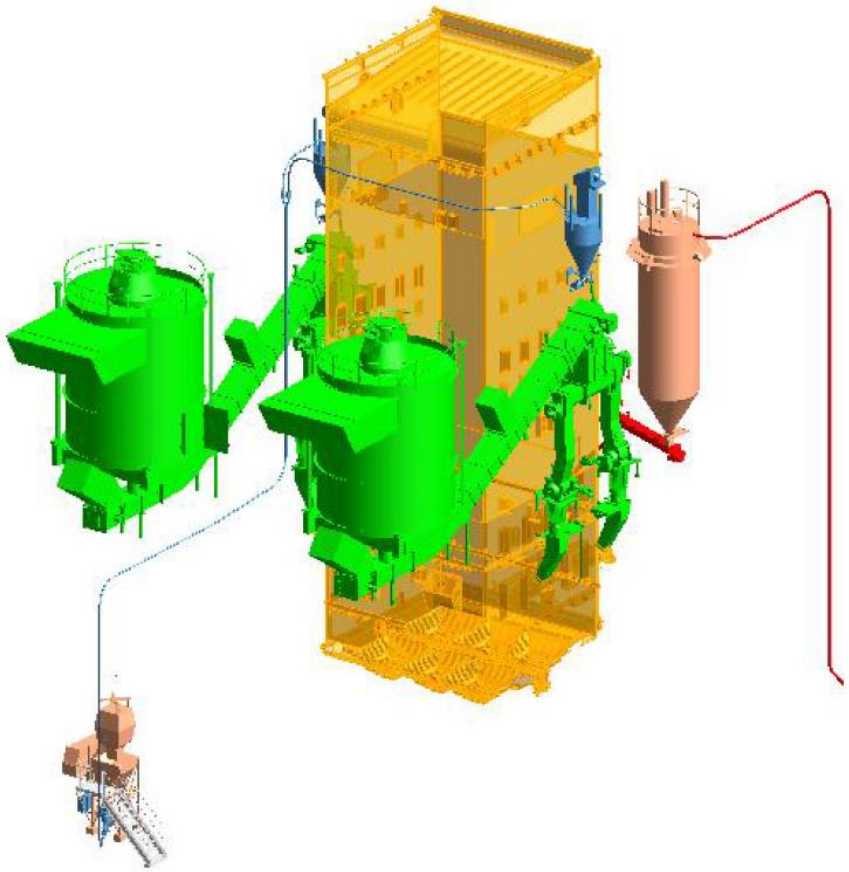

Figure 9. Sulphur- sand and fuel feed system. [20.]

The following sections will describe the sulphur feed system in more detail.

5.1.1 Outdoor bag silo and feeding system

An outdoor sulphur feed silo is put to an easily accessible location outside the power plant building. Sulphur is brought here in big bags, which one at a time is fed into the equipment according to consumption. The size of the feeder is about 1 cubic meter and the sulphur consumption is continually monitored from the flue gases. Also included comes a dust control unit and on top of the silo is an X-beam with a crane with which it is easy to move bags into the silo.

5.1.2 Pneumatic transport system, RPC60

A pipeline is built from the feed silo into the top of the boiler, from where the sulphur is equally distributed to the screw feeder of the fuel feeds. The transportation capacity of the system is about 1 m^3 / hour or 1100 – 1400 kg per hour.

The instantaneous transportation capacity of the system is 60 l with a structural pressure of 8 bar and it is equipped with control and maintenance valves. The system comes supplied with a local control unit that controls the solenoid valves and pressure selectors. The unit is a Siemens S7200 - controller.

5.1.3 Transportation pipeline

The line stars from the feed silo and rises through the outside of the building approximately to the level of the top of the boiler. It starts with a straight pipe about 45 meters long per line and it has 4 long turns. Y-intersections with two fully opening controllable ball valves. Control unit with message lights and start buttons.

5.1.4 Feed system and screw feeder

The screw feeder dispenses sulphur according to the feed instructions, which either automatically calculated or values can be set by the operator.
The feeder of the feeding system is made of stainless steel with a volume of 2.5 m^3.

Screw feeders, diameter 50 mm, feeding capacity 2.3 – 23 kg per hour made of stainless or construction steel. 0.18 Kw motor with the feeding valves pneumatically activated.

6 Environmental permit

Growing environmental and health consciousness has risen the need to follow the emissions of industrial power plants. During the 20th - century, the growing economy and fast industrialization generated many very polluting industrial facilities and power plants to meet the energy demands of the industry. This caused very polluting local atmospheric emissions, and at the time information and knowledge about air pollution not high. The great smog of London and other corresponding events are a prime example of rising worry about such events. After that, a lot of research has been devoted to the industrial emissions and today flue gas cleaning systems are very effective and a lot of resources and control are directed at mitigating air pollution.

The industrial emissions directive set by the European Union affects all member countries. The directive (IED) 2010/75/EU sets goals to protect the environment and human health for the member countries. This happens through regulating environmental permits of the industrial facilities. [20.] Nationally, Finland also has an environmental law 86/2000 [21.] which has now been revoked by law 527 / 2014. In the clause § 1 of this law it is prescribed that environmental degradation and the threat of that has to be mitigated, emissions reduced, a healthy and pleasant environment has to be guaranteed and sustainable utilization of natural resources has to be promoted. [22.]

Industrial emissions - directive withholds the following directives: [20.]

- IPPC-directive
- LCP, large combustion part directive
- Waste combustion directive
- Industrial VOC - directive
- A directive to control titanium oxide industry

The industrial emissions directive emphasizes the utilization of BAT - policies when doing technology choices, and BAT - conclusions are of key importance when it comes to environmental emissions.

This company has acquired an environmental permit from the Finnish environmental institute given in 2007. [2. p, 5] Another application for the renewal of the environmental permit is on the way, and there is a comprehensive description about the plant activi-

ties, the types of products that are created and the effects the activities have on nearby environment, local air quality and aqueous effects. The plant is not situated in a groundwater area nor are there wells meant for household consumption in the vicinity. [2. p, 7] The prime environmental effects of the plant come from the flue gases, which are created as the reaction products of combustion. Right next to the power plant is the Lahti highway, and another important source of local air pollution is small-scale combustion in households. The solid particles created during combustion move with flue gases and are separated within the power plant by an electrostatic precipitator. Nevertheless, the most significant emissions are flue gas emissions, and the main components are carbon dioxide, sulphur dioxide, nitrous dioxides and particles. Operating the plant creates about 7000 tons of fly- and bottom ash in a year. This can, however, be utilized in useful purposes, such as excavation. [2. p, 6] Considering that the plant is located right next to a highway and that the plant is situated in an industrial area with the Sinebrychoff factory, the noise pollution caused by the plant is of no ill consequence to local population.

Uusimaa center for transport and environment guides the local air quality control. In the year 2012 the company participated into a co-operative group, where there were representatives of the nearby municipalities, HSY and from the center. Local air quality was observed by this group with a movable measuring station in years 2005 and 2010. The plant is situated about 8 km from the center of Kerava and the air quality in the aforementioned years was found to be good or satisfactory for 95 % of the year. The quality was tolerable about 4 % of the time. The quality was rated poor or very poor for about 1 % of the hours in a year. The main reason for this was dusty conditions of the street, but occasionally also the rise in the level of nitrogen oxides. In general, the concentrations of nitrogen oxides and breathable particles were clearly below threshold limits. [2. p, 7]

The environmental permit has a clause titled ‘Chemicals’ in section 8.2. [2. p, 11] This section has all the information about the chemicals used at the power plant, and if the sulphur feed system is to be implemented, then the chemicals used in the system must be added here. The sulphur silo and its possible effects must be added to the environmental permit and the necessary material safety data sheets, which can be found in the appendices of this thesis. The sulphur content of the flue gases must not exceed the upper tolerable limit given in the environmental permit, and the sulphur feed is controlled and monitored by either the operator or automatic control unit. These changes

must be mentioned in the permit. According to Table 4 on page 13 of the environmental permit, in year 2013 the atmospheric sulphur dioxide emissions were 9 tons, or 16 mg / nm^3. And this was only for the fossil fuels. On page 16, the proposed limits for threshold values are the following:

- Sulphur dioxide 240 mg/m^3 (n), 6 % O_2
- Nitrogen oxides 300 mg/m^3 (n), 6 % O_2
- Particles 30 mg/m^3 (n), 6 % O_2

However, this sulphur dioxide limit is based on the fuel ratio which has 40 % peat and 60 % of wood chips. This will change according to the actual used ratios of fuels and whether sulphur will be mechanically fed into the furnace.

The new SuPo - legislation will not bring any changes to emissions monitoring with plants which have a thermal power below 100 MW. The emissions will be measured periodically in the future, as they are measured now. [2. p, 16]

7 Conclusions and remarks

According to a research done by VTT, it would be good to burn 10 - 30 % of peat with wood, or other sulphur-containing fuel with wood, to reduce the bed agglomeration problems and formation of alkali chlorides on superheater surfaces. It has been shown, that with wood chips it would be good to use peat with even a 30 - 40 % ratio. Also for combustion of peat there are synergy benefits when wood chips are combusted in co-combustion. [22. p, 3] For peat power plants, sulphur emission threshold limits are usually 350 mg / m^3, and reaching this requires the use of lime for sulphur binding.

A possible area for further study would be whether the feeding of elemental sulphur would also have wished effect as peat combustion because during peat combustion, a considerable amount of other compounds and peat is released, which changes the reactions mechanisms and reaction products.

The relation between the behavior of ash and the composition of the fuel's chemical elements is important, if there is a wish to avoid problems during active operation of the plant. The problems with ash are also related to its phase changes. Fully or partly

melted ash is very sticky, and it causes corrosion on heat surfaces and agglomeration. Ash is very sticky if it is in at least 15 % liquid form.. The melting temperature of ash is especially affected by alkali metals. [14. p, 28 - 29]

When the fuel has also sulphur in it, the alkalis sulphate and cannot any more react with chlorine to form alkali chlorides. The chlorine is thus released as hydrogen chloride and transported with the flue gases out of stack without causing problems. [23. p, 60]

Sulphur containing compounds also have a way of forming ash deposits on heat surfaces, which increase the melting point of the deposits. This elevated melting point prevents the slagging of ash; as a result, additional layers cannot be formed and fouling is clearly decreased. The injection of sulphur granules can also reduce agglomeration. [23. p, 18]

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Title of the Appendix

SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 5.1 Revision Date 07.12.2012
Print Date 18.11.2014
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifiers

Product name : Sulfur

Product Number : 213292
Brand : Aldrich
Index-No. : 016-094-00-1
CAS-No. : 7704-34-9

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Finland Oy
Bulevardi 7
FI-00120 HELSINKI

Telephone : +358 9 350 9250
Fax : +358 9 350 92555
E-mail address : eurtechserv@sial.com

1.4 Emergency telephone number

Emergency Phone # : Myrkytystietokeskus 358 9 4711

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 [EU-GHS/CLP]
Skin irritation (Category 2)

Classification according to EU Directives 67/548/EEC or 1999/45/EC
Irritating to skin.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008 [CLP]
Pictogram

Signal word Warning

Hazard statement(s)
H315 Causes skin irritation.

Precautionary statement(s) none

Supplemental Hazard Statements none

According to European Directive 67/548/EEC as amended.
Hazard symbol(s)

R-phrase(s)
R38 Irritating to skin.

http://www.sigmaaldrich.com/safety-center.html

Title of the Appendix

Content of the appendix is placed here.